Controlling the dynamics of quantum mechanical systems using meta-atoms

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Abstract

We provide an overview of our latest activities on using optical meta-atoms to mediate the interaction of light with molecular systems. The first subject concerns the control of the dynamics of quantum mechanical systems featuring dipole-forbidden transitions. There, the meta-atoms provide local fields that exhibit a large electric quadrupole moment. The second issue is related to the enhancement of the upconversion process in erbium-doped glasses. There, the optical meta-atom has to show a resonance at multiple frequencies which matches the term schema of erbium. It will be concluded that optical meta-atoms are promising to enable inaccessible processes in a quantum mechanical system which will allow groundbreaking applications.

1. Introduction

Optical meta-atoms are metallic nanostructures with complex geometries that provide a desired resonant scattering response. Optical meta-atoms are the basic building blocks of metamaterials upon closely packing them. The study of the peculiarities of optical meta-atoms is essential to gain insight into achievable bulk properties of metamaterials. However, already individual structures attracted considerable research interest in the past. Optical nanoantennas, as they are usually dubbed then, promise to provide electromagnetic fields on the nanoscale with predefined spatial and spectral characteristics. A prominent class of applications of optical nanoantennas consists in mediating the interaction of light with other nanoscopic systems. Here, we detail two applications in that field of research from our recent work. The first one is the ability to strongly excite dipole-forbidden atomic transitions usually discarded since their interaction with light in free space is negligible [1]. The second one is the enhancement of the upconversion process which will find use for the photon management in future solar cells. Unique to our work is a rigorous analysis of the optical properties of the meta-atoms and the treatment of the entire dynamics in the molecular and/or the atomic system on the base of rate equations.

2. Modified dynamics of atomic systems sustaining dipole forbidden transitions

The ability of optical nanoantennas to enhance electric quadrupolar transitions has been demonstrated [2]. Such quadrupolar transitions are usually negligible for atoms or molecules in free space since their excitation is intimately linked to strong field gradients. Such gradient is marginal because the free space wave length exceeds by far the molecule size. This long standing paradigm can be lifted. As shown in Fig. 1,for a nanoantenna made of two closely spaced silver nanospheres the local electric quadrupole contribution can be enhanced by six orders of magnitude compared to free space. The radius of the nanospheres is 30 nm and their separation is 3 nm, respectively. The dimer is illuminated by a linearly polarized plane wave at a wavelength of 437 nm propagating parallel to the connecting line of

ISBN 978-952-67611-2-1

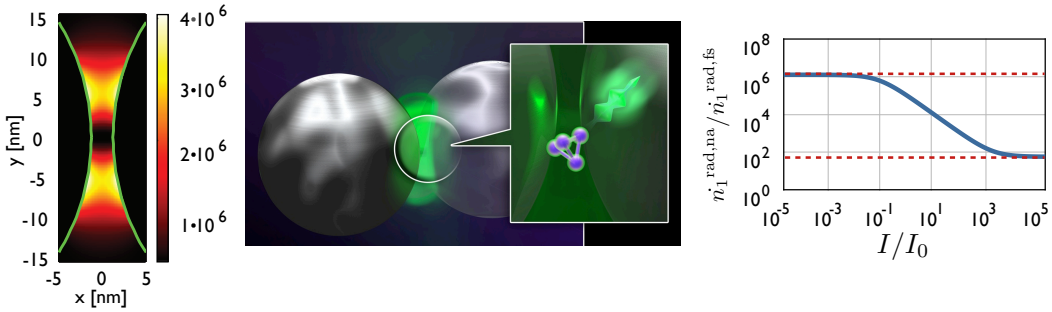

Fig. 1: (left) Enhancement of the local electric quadrupole contribution when compared to free space in a cross-sectional plane between two nanopsheres.(middle) Artistic view of the scenario. (right) The dipolar emission of a molecule from a state into which a quadrupolar excited state decays non-radiatively. The red lines correspond to analytical expressions for limiting cases of either strong or weak pump intensity.

the dimer. This enhancement can be anticipated to overcompensate the lower transition probability of electric quadrupolar transitions. They are estimated to be $10^{-5} - 10^{-7}$ times smaller than the transition probability of electric dipolar transitions. To make use of such enhancement in a possible experiment, a molecule is assumed to be placed between the dimer [middle of Fig. 1]. The system is pumped at the frequency of the simulation in Fig. 1, i.e. 2.84 eV. The molecule is assumed to have a quadrupolar transition at this frequency. The excitation shall subsequently quickly non-radiatively decay to an intermediate level from where it decays radiatively into the ground state by an electric dipolar transition. This emission of dipolar radiation is suggested to be used as the observable that allows to conclude on the enhancement of the quadrupolar transition. The considered term schema resembles those of s- to d-orbital transitions of alkali metals. All characteristic parameters, such as the ladder spacing and the life times of the states are chosen as to be representative. The right of Fig. 1 shows the enhancement of the dipolar emission as a function of the pump intensity. Normalization is made with respect to the saturation intensity of the quadrupolar transition. It can be clearly seen that the enhancement promises indeed to overcome the inefficient excitation of quadrupolar transitions and makes their strengths comparable to that of electric dipolar transitions. This, however, applies only in the weak intensity limit. For intensities above the saturation intensity, the process is limited by the enhancement of dipole emission at the last radiative level. In both limiting cases analytical approximate expressions can be derived. The entire functional dependency has been obtained while solving for rate equations describing the three-level system in the steady-state condition. Details thereof will be outlined in-depth at the conference. Despite these saturation processes we wish to stress that the promise to enhance quadrupolar transitions of atoms and molecules to a strength where they tend to be comparable with the usually exclusively considered electric dipolar transition, is expected to have a have a tremendous impact on potential spectroscopic or sensing applications.

3. Enhancement of upconversion processes in trivalent erbium

Another application lies within the field of photon management for solar cells. For instance, optical nanoantennas can significantly enhance the efficiency of rare earth materials that shall upconvert the light by providing an enhanced density of states at specific frequencies. This allows to utilize sub-band gap photons of the silicon solar cells which are otherwise lost. However, as can be seen in the term schema of trivalent erbium shown in Fig. 2 that is considered, various energy levels are involved and the nanoantenna has to accommodate the goal of enhancing the transition probabilities at various frequencies. The problem, however, is less severe, and it can be shown on analytical grounds that only two frequencies are particularly relevant. In our analysis we combined a sophisticated rate equation model for the upconversion dynamics with the simulations of the simulation of the nanoantenna [3].

ISBN 978-952-67611-2-1

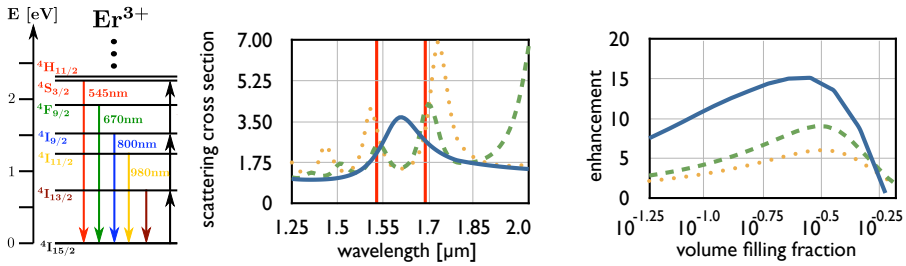

Fig. 2: (left) Term schema of trivalent erbium. In the upconversion of light to a frequency that is larger than the electronic band gap of silicon, various processes are involved. However, the sequence of an absorption from a $I_{15/2}$ to a $I_{13/2}$ state at 1523 nm followed by an excited state absorption or energy transfer processes to $I_{9/2}$ at 1680 nm and a multi-phonon relaxation into the $I_{11/2}$ with a final radiative decay into the $I_{15/2}$ state is most beneficial. (middle) Scattering cross sections of three nanoantennas that posses resonances at the desired frequencies (red lines). The blue-solid curve is a gold core-shell sphere sustaining an electric dipolar resonance. The other curves correspond to core-shell spheres sustaining pairs of higher order resonances. The multipoles orders correspond to $l = 3$ and $l = 4$ for the green-dashed and to $l = 4$ and $l = 5$ for the yellow dotted curve. (right) Enhancement of the upconversion luminescence depending on the volume fraction of the nanoantennas.

Various nanoantennas, which fulfill this requirement, can be designed. However, they possess different spatial mode profiles which additionally have to be considered. As can be seen in Fig. 2, it turns out that the most feasible structure sustains an electric dipolar resonance. Only for an excessively large volume filling fraction nanoantennas sustaining higher-order resonances are beneficial. However, since the area occupied by the nanoantennas does not contain upconverting material, an intermediate filling fraction is favorable. For this reason, nanoantennas with spatially less localized modes, i.e., the electric dipole mode, are preferable. It is important to emphasize that the upconversion luminescence is enhanced by more than one order of magnitude in comparison to the efficiency of a pure upconverion material. Moreover, the efficiency is also enhanced by roughly one order of magnitude compared to the enhancement induced by a solid nanosphere that has been already considered in such analysis.

4. Conclusion

In conclusion, we wanted to stress that optical nanoantennas are preferable devices to affect molecular dynamics. Our main contribution is the consideration of molecular processes beyond isolated electric dipolar transitions which are usually at the focus of interest. The associated involved processes require optical nanoantennas to provide electromagnetic fields with more sophisticated constraints. Strong field gradients were shown to be of use in order to trigger intra-molecular processes that are usually too weak to be of any concern in free space. Resonances at multiple frequencies are finally desirable if molecular processes shall be enhanced where multiple transitions are involved. All these things need to be considered and are outlined in much more detail at the conference. The required nanoantennas resemble meta-atoms which sustain resonances at multiple frequencies and/or resonances which are characterized by higher order multipole moments. Such meta-atoms are currently accessible either by bottom-up or top-down approaches and will find use in future metamaterials.

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